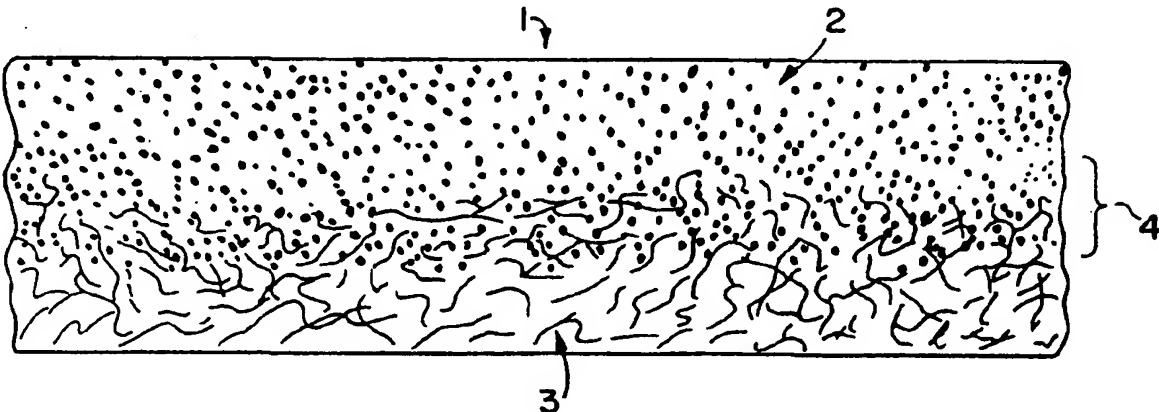




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(54) Title: BATTERY SEPARATORS  (57) Abstract <p>A battery separator composed of a microporous, composite sheet product having first and second major surface, formed from a uniform mixture of a polymer, a filler, a processing aid, a porous form stable layer at least partially embedded in either the first or second major surface. The weight ratio of polymer to filler is from about 1:4 to 1:50; preferably about 1:4 to 1:10.</p>		

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BATTERY SEPARATORS

This application relates to microporous sheet products, such as battery separators and batteries containing such separators.

BACKGROUND OF THE INVENTION

The subject invention is directed to a sheet product which is useful as separator components for batteries and to improved batteries containing the formed separator. More specifically, the present invention is directed to a thin, microporous sheet product composed of a highly filled polymeric matrix having a porous support layer at least partially embedded in the first, second or both major surfaces of the sheet product.

Membranes have been formed from various materials and used in various applications such as in ion exchange, osmotic and ultra filtration devices including desalinization, kidney dialysis, gas separation and other applications. Macro and microporous membranes have been used as a means of insulating and separating electrodes in battery devices. Each application provides an environment and a set of desired parameters which are distinct to the specific application.

Storage batteries have at least one pair of electrodes of opposite polarity and, in general, have series of adjacent electrodes of alternating polarity. The current flow between these electrodes is maintained by an electrolyte which may be acid, alkaline, or substantially neutral depending upon the nature of the battery system. Separators are located in batteries between adjacent electrodes of opposite polarity to prevent direct contact between the oppositely charged electrode plates while freely permitting electrolyte movement and ionic transfer. Separator components have taken many

- 2 -

forms. In a modern battery design, the separator is in the form of a thin sheet or film or more preferably, a thin envelope surrounding each electrode plate of one polarity.

It is generally agreed that one of the critical elements in a battery design is the separator component and, to be highly effective in the design, the separator should have a combination of features. The battery separator must be resistant to degradation and instability with respect to the battery environment, including the other battery components and the battery chemistry. Thus, the battery separator must be capable of withstanding degradation of strong acids (such as sulfuric acid commonly used in acid battery designs) or strong alkali (such as potassium hydroxide used in alkaline battery designs) and to do so under ambient and elevated temperature conditions. Further, the separator should also be of a thin and highly porous character to provide a battery of high energy density. Although battery separators of thick or heavy design have been utilized in the past, such materials detract from the overall energy density of the battery by reducing the amount of electrodes and/or electrolyte that can be contained in a predetermined battery configuration and size. Another criteria is that the battery separator must be capable of allowing a high degree of electrolyte movement. Stated another way an effective separator membrane must exhibit a low electrical resistance when in the battery. The lower the electrical resistance the better the overall battery performance will be. A still further criteria is that the separator should be capable of inhibiting

SUBSTITUTE SHEET (RULE 26)

- 3 -

formation and growth of dendrites. Such dendrite formation occurs during battery operation when part of the electrode material becomes dissolved in the electrolyte and, while passing through the separator, deposits therein to develop a formation which can, after a period of time, bridge the thickness of the separator membrane and cause shorting between electrodes of opposite polarity.

In addition to meeting the above combination of properties, it is highly desired to have a sheet product which is capable of exhibiting good physical properties of tensile strength, puncture resistance, flexibility and ductility to withstand the handling and processing without developing imperfections and cracks which would cause the sheet product to be unsuitable as a battery separator. Meeting this criteria is contrary to some of the above described properties (i.e. thin and light weight material with high porosity to provide good ion permeability vs. high strength, puncture resistance, and flexibility). In providing envelope type separators, these physical properties must also be accompanied by the ability of the material to be sealable by heat, pressure welding, or other means so as to provide an envelope design.

Moreover, recent changes in the manufacture and assembly of electrodes, enveloped electrodes and batteries are setting a higher level of performance standards for separators.

For example, new electrodes are being formed of an expanded metal grid on to which the electrode paste is placed. The grid is then cut to length and dried. The cut edges of the grid leave sharp points or edges which can pierce the edge of a separator, even when formed into an envelope. Likewise, the electrode plates are stacked, blocked, compressed and placed automatically into the battery case. Uniformity of the

SUBSTITUTE SHEET (RULE 26)

enveloped electrode is important. Moreover, the separator must be able to withstand the physical abuse generated by assembly of the separator into the battery. Further, batteries are being packed in higher densities, leaving less free room for electrolyte. Lastly, recombination batteries which use absorbed electrolyte instead of free electrolyte also place an additional burden and requirement on separators. It would be desirable for separators to contain or carry a volume of electrolyte to ensure that the electrodes are kept in constant contact with electrolyte and operate at peak efficiency and to have a high level of porosity to aid in gas movement. Further, it is desirable to have a structure which has a variety of pore diameters to allow for maximum gas transfer.

Various microporous membranes or sheet materials have been suggested for utilization as a battery separator. Separators conventionally used in present battery systems are formed of polymeric films which when placed in an electrolyte or an electrolyte system, are capable of exhibiting a high degree of conductivity while being stable to the environment presented by the battery system. The films include macroporous as well as microporous materials. The porosity permits transportation of the electrolyte. Examples of such separators include polyolefin sheets which have been stretched and annealed to provide microporosity to the sheet, such as is described in U.S. Patents 3,558,764; 3,679,538; and 3,853,601. In addition, other separators which include filler materials are disclosed in U.S. Patents 3,351,495 and 4,024,323. Such separators contain one or more polymers, fillers and processing aids. The ratio of polymer to filler by weight is typically limited to 1:2 to 1:3 as it has been found that when the filler is increased over that amount, the resultant separator loses its strength and flexibility,

- 5 -

tending to fall apart during separator formation and battery assembly. Further, current separators tend to shrink during processing, most notably during the extraction of processing aids. This leads to a reduction in usable material for a given amount of raw materials. Additionally, in those instances where little or no filler is used, the porosity can be lost and only reestablished by stretching the shrunken sheet back to its desired size.

Various methods have been used to counter or compensate for this shrinkage, including forming unextracted separators in larger sizes which, upon extraction, result in the desired size, thickness and configuration and/or the use of processing aids and solvents for them which minimize the shrinkage that occurs. The former method requires the use of additional raw materials, while the latter requires the use of less effective solvents (such as water) and therefore longer and less efficient extraction processing or the use of chlorinated solvents which are unacceptable and highly controlled due to environmental (ozone depletion) and health and safety (potential carcinogens) considerations. These separators exhibit electrical resistance, physical strength or other properties which do not permit the formation of a highly efficient, high energy battery system.

It is highly desired to have a battery separator which is capable of exhibiting very low electrical resistance while at the same time providing the combination of properties described above and which is capable of being manufactured and processed on existing equipment.

SUMMARY OF THE INVENTION

The present invention is directed to a sheet product, battery separators formed therefrom, electrodes separated by such separators and to improved batteries

SUBSTITUTE SHEET (RULE 26)

- 6 -

which incorporate the thus formed battery separators. The subject separator is a composite formed of a microporous sheet product composed of a substantially uniform mixture of thermoplastic polymer and filler present in a ratio by weight of from about 1:4 to 1:50 preferably 1:4 to 1:10, more preferably 1:6 to 1:10 and said sheet product has a porous form stable layer embedded at least partially therein. The separator is capable of being formed in existing equipment and by existing processes with minimal modifications to either.

IN THE DRAWINGS

Figure 1 shows a cross sectional view of a sheet product according to the present invention.

Figure 2 shows a cross sectional of a second preferred embodiment of the present invention.

DETAILED DESCRIPTION

The present invention provides a flexible sheet material having high void volume, porosity of a microporous nature and of a configuration which substantially inhibits dendrite formation. The subject sheet material has high tensile strength and ductility sufficient to withstand handling during battery formation, is capable of being formed into desired shapes for use in a battery, is capable of exhibiting a high degree of stability to the battery environment over sustained periods of time such as oxidation resistance and high temperature resistance and of allowing a high degree of electrical conductivity (low electrical resistance). Still further, the subject sheet material has the ability to maintain its integrity and performance characteristics while being able to be formed into a enveloped design separator.

SUBSTITUTE SHEET (RULE 26)

- 7 -

For purposes of clarity, certain terms used in the present description and in the appended claims have the following meanings:

A "battery" refers to a single electrochemical cell or, alternatively, a multiple of electrochemical cells which are designed to operate in coordination with each other.

A "separator" is a component of a battery which provides a means of separation between adjacent electrode plates or members of opposite polarity. The separator of the present invention may have various configurations, such as a flat, embossed or ribbed material in the form of a membrane or an envelope design capable of maintaining separation between electrodes.

A "form stable layer" is a material, such as a sheet or mat which is dimensionally and physically stable in its length and width during processing and use.

A "sheet product" is intended to define a composite product of the present invention which is microporous, has a porous form stable layer at least partially embedded within the sheet product's thickness and has a form of a polymer-filler composite with or without the presence of a processing aid. The sheet product can be used to form separators suitable as a battery component.

The term "ultra high molecular weight polymer" is intended to define a polymer having a weight average molecular weight of at least about three million, preferably at least about four million, as determined according to ASTM D-4020 or DIN-53493 or by the Zero Tensile Strength Test (ZST) as having a value of at least 0.1, preferably 0.1 to 1 (Newtons/mm²), more preferably between 0.2 and 0.6 N/mm².

Figure 1 shows a cross sectional view of a sheet product 1 according to the present invention.

SUBSTITUTE SHEET (RULE 26)

- 8 -

The sheet product is bound by two major surfaces formed of two distinct layers therebetween. The sheet product is a microporous polymeric matrix 2 composed of a substantially uniform composition formed of a polymer and an inert filler, wherein the ratio of polymer to filler (wt.) is from about 1:4 to about 1:50, preferably 1:4 to about 1:10 more preferably 1:6 to 1:10. The layer also contains from 0 to 25% by weight of the components of the matrix of a processing aid such as mineral oil. The sheet product, in addition, contains therein a porous, form stable layer 3, being at least partially embedded into one of the two major surfaces of the matrix as shown at the interface 4 between the two layers 2 and 3. The sheet product of the present invention should be in the form of a thin sheet of less than 50 mils (1.27 mm) and preferably less than 10 mils (.254 mm) in thickness measured as a back web thickness when ribs are present.

The composition of the resultant sheet product will depend upon the components used, their respective ratios and the degree of extraction of the processing aid and/or filler. The processing aid can be completely removed, leaving a highly filled polymeric sheet product or, alternatively, can have at least 60 percent and, preferably, 85 percent of the processing aid of the admixture removed. These products normally show good retention of physical properties, as well as good electrical stability and oxidation resistance. The microporous matrix of the sheet product normally has from about 5 to 25 percent (by weight) of the polymer mixture, about 8 to 95 percent filler, and from about 0 to 20 percent processing aid. More preferably the microporous plastic matrix comprises a mixture of from 15 to 25 percent polymer, 75 to 85 percent filler, and from 0 to 10 percent processing aid.

SUBSTITUTE SHEET (RULE 26)

- 9 -

The resultant sheet product is a microporous sheet of very high porosity (porosity of at least 50 vol. percent, preferably greater than 60 vol. percent and even up to 98 vol. percent in some embodiment).

Very thin, flexible sheet products having good mechanical properties of tensile strength, ductility, high porosity and oxidation resistance have been unexpectedly formed.

The sheet product is a flexible material capable of being folded upon itself and formed into an envelope design. This is surprising in view of the high amount of filler contained in the present composite separator. Logic argues that the product should be stiff, brittle and inflexible. Yet the combination of the elements of the present invention provides a flexible, conductive product that can be easily folded.

The sheet product can be cut into suitable shapes to be used as a separator between electrodes of a battery such as a leaf separator. The separator should extend the full length and width of the electrode to prevent electrodes of opposite polarity from contacting one another. In certain instances, it is preferred that the separator be void of patterns, ribs or other raised sections, e.g. flat sheet (generally for alkaline batteries) or may contain raised portions, such as ribs, buttons or the like (generally for acid batteries). The ribs or other raised portions can be formed from the polymer/filler of the sheet or from any polymeric material capable of adhering to the polymer used to form the base sheet product.

The instant process and compositions produce microporous battery separators which exhibit low electrical resistance, which readily permits electrical conductivity via the electrolyte, and which possess excellent tensile properties to accommodate the various

SUBSTITUTE SHEET (RULE 26)

- 10 -

physical forces encountered in the battery during production and operation. In addition, the present separator exhibits a high degree of stability and lack of degradation to the various chemical and electrochemical forces encountered in the battery.

A further improvement of the present invention is that the material is dimensionally stable, both during processing and use. Typically, plastic separators undergo some shrinkage during processing and use. For example, it has not been uncommon for separators formed of plastic and an inert filler to undergo a 10% reduction in width and length during extraction of the processing aid. This results in reduced porosity and reduced yield. Similarly, shrinkage is known to occur in the finished battery after the separator has been formed as an envelope around the electrode. Shrinkage in the battery exposes portions of the active material which may fall off or dry out or in the worst case contact an electrode of opposite polarity causing a short.

The sheet product of the present is dimensionally stable both during processing and use. Typically, the sheet product will shrink less than 3%, in both length and width, more typically less than 1%, depending upon the material of the form stable layer and its inherent tendency to shrink.

In addition to dimensional stability, the present invention also has high tensile strength. This is particularly useful in the formation of the product such as when a processing aid is being extracted, during processing of the product into a battery and during use. For example, in alkaline batteries the separator is often spirally wrapped with an electrode into a "jelly roll" configuration. Having a strong, material that is dimensionally stable and having high strength is

SUBSTITUTE SHEET (RULE 26)

- 11 -

desirable as it tends to eliminate the problems of breakage or stretching of the separator during the winding operation. Likewise, in acid batteries the enveloping of electrodes is becoming more and more automated. Having a high strength, dimensionally stable material allows for better and more consistent feeding and tracking of the separator material through the automated process. Lastly, the tensile strength also provides improved resistance to puncture by parts of the battery, such as exposed portions of the grid, or by the assembly equipment. It also provides better resistance to cracking which may occur in separators which are folded and/or bonded together, especially into envelopes.

Another advantage of the present separator is its ability to withstand oxidation and degradation caused by consistent high temperature usage. It has been found that the present separator will provide superior resistance to degradation caused by use of the battery at high temperatures (such as 70°C) than is possible with currently available products. This is important as more and more applications are experiencing higher use temperatures. For example, as automobiles are being redesigned ("cab forward" and other such designs) the room and air circulation in the engine compartment is becoming less and less, thus causing the average operating condition temperatures to increase. Such conditions place a severe strain on batteries and tend to cause a premature and rapid oxidation of the separators which lead to cracks, holes and dendritic growth which cause battery failure. By providing a separator with superior physical resistance to such conditions, one is able to provide a battery that can meet the changing use conditions that are occurring today.

SUBSTITUTE SHEET (RULE 26)

- 12 -

A further unique feature of the present invention is the pore structure within the composite structure.

The pore structure is unique in that a number of separate, distinct pore types are formed. In the microporous layer, the pores are typically a microporous channel or tunnel of an average diameter of less than 1 micron as is typically found in microporous plastic separators. The pore structure in the form stable layer is macroporous generally of an average diameter of at least of about 1 micron, generally about 10 microns and are formed between the overlaying and adjacent fibers. The pores formed at the interface between the form stable layer and the microporous plastic matrix are microporous, but are formed as extended elongated pores formed along the length of the fibers which typically form the form stable layer. This is particularly so where the materials of the microporous layer and the form stable layer are different. For example, when the polymer is a thermoplastic, preferably a polyolefin and the form stable layer is formed of glass fibers, it has been found that the two materials are typically hydrophobic and hydrophilic (respectively) and therefore do not bond to each other readily. Rather, it is believed that the two materials tend to intermesh or entangle themselves within the other. This leads to the formation of these unique extended, elongate pores in the interface area. The pores are particularly suited for the retention of electrolyte within the separator. This is of particular interest to one in the battery field as it allows for the inclusion of more electrolyte in a given battery space than had previously been available. The increase in electrolyte allows for higher storage capacity and reserves, thus providing a better, stronger battery than had been previously available.

SUBSTITUTE SHEET (RULE 26)

- 13 -

Moreover, this pore structure is also useful when the form stable layer is placed against the face of the negative electrode. The negative electrode should be constantly in contact with electrolyte, however in actual practice as the flat side of the separator (if ribbed the ribs face the positive electrode) is adjacent the negative electrode, there is little area for the presence of electrolyte. If the electrolyte were to be excluded from contact with the negative electrolyte, the plate can dry out and become inactive. Even upon rewetting, the electrode never fully regains its capacity. By having the form stable layer adjacent the negative electrode, electrolyte retained within the extended, elongate pores can be easily supplied to the negative electrode, making the chance of its drying out less likely. Additionally, the form stable layer being porous itself acts as an additional reservoir and as a spacer for electrolyte flow adjacent the negative electrode.

Additionally, the present invention provides one with a multimodal pore size distribution. Typically plastic microporous separators have a single mode of pore size ranging from about 0.5 micron to about 1 micron. Fibrous separators have a separate, distinct monomodal pore size of about 10 microns. The present invention due to its composite structure and high filler content provides a multimodal, typically a trimodal pore size distribution with a first mode of large pores being above 10 microns, a second mode of pores being about less than 1 micron and a third mode of pores being about less than 0.5 micron which represents the porous structure of the filler itself. All of these different pore sizes contribute the unique high porosity and electrolyte retention which the present invention exhibits.

SUBSTITUTE SHEET (RULE 26)

- 14 -

One embodiment of the present invention is as a leaf separator, i.e. a form stable sheet type of separator which is placed between electrodes of opposite polarity. The product of the present invention is well suited for this application.

Another preferred embodiment of the present invention is as a flexible, thin, foldable separator which can either be formed as an envelope around an electrode or run over and under a series of electrodes of opposite polarity so as to separate them from each other.

A third preferred embodiment of the present invention is as a separator for recombination type batteries. In recombination batteries, oxygen is generated as a result of the charge/discharge cycles and travel from the positive to the negative electrodes to create the reactions. The electrolyte is either present in minimal amounts (starved systems) or as a gel (gel systems). The separator must be capable of having high porosity, greater than 85%, more preferably, greater than from about 90 to 98% most preferably 95%. Further, it must also be capable of allowing the movement of the gases through it. Lastly, it must be capable of absorbing and holding a large amount of electrolyte as there is little, if any excess electrolyte present (unlike tradition "flooded" lead acid batteries). In this embodiment the use of polymer/filler ratios of from 1:20 to 1:50, preferably 1:30 to 1:50 provides all of the necessary characteristics.

In another embodiment, the separator is used in an alkaline battery and is formed around the electrode as wrapping (prismatic and jelly roll wrappings are well known).

- 15 -

A further embodiment of the present invention is to form a composite battery separator which is applied directly to the surfaces of an electrode plate (positive or negative) during plate formation. This is unlike the traditional process today where a separator is formed as an envelope or placed as a leaf between already formed electrodes. By attaching the separator to the electrode during electrode formation, one can eliminate the additional step of separator placement. Additionally, by having the separator applied directly to the electrode plate, one may be able to limit the amount of dusting and active material fall off that occurs today with the handling of the dry electrode plates between its formation and separator placement.

Preferably, the exposed surface of the porous form stable layer is placed against and/or partially embedded into the two major surface of the electrode after its formation (by the application of a wet paste or slurry of active material to an electrode grid), but prior to its drying. By doing so, one causes the separator and electrode to bond together. Either a single piece of the composite separator may be folded around the electrode or separate separator layers may be applied to each of the two major surfaces of the electrode.

In this embodiment, it is preferred that the form stable layer be formed of a glassmat, as the glass is best suited for the highly oxidative environment associated with the electrode and its formation.

The electrode grid may be in an individual form on to which active material is placed and then a separator is attached to the active material. Alternatively, it may be formed as a continuous expanded metal grid which after having the active material and separator laminated to it is then cut to the desired

SUBSTITUTE SHEET (RULE 26)

- 16 -

size. In the latter embodiment, it may be desirable to seal any exposed side or bottom edge, either with a separate strip of material or a coating such as of a rubber latex or a hot melt thermoplastic.

Another embodiment of the present invention provides a battery separator having low content, 0 to about 20 weight percent, preferably from 0 to about 10 weight percent of residual processing aid. It has been unexpectedly found that the majority or all of the processing aid can be removed and yet still function as a separator and not fall apart due to oxidation. This is a complete reversal from the separators formed today wherein oxidation resistance is dependent upon the amount of processing aid present within the separator. When such a low processing aid content sheet product is formed, as according to the present invention, the resultant separator is capable of maintaining its high void volume, exhibits low electrical resistance when in the battery system, exhibits high tensile strength and exhibits superior oxidation resistance.

The polymer used to form the body of the sheet product of the present invention can be selected from polymers which are stable with respect to a battery environment for which the sheet product will be used. That is to say, the polymer must be free from being attacked and decomposed by the components making up the battery environment. For example, the polymer must be stable to strong acid when contemplated for use in an acid battery (i.e. lead-acid battery using a sulphuric acid as electrolyte) or to strong alkaline environment when contemplated for use in an alkaline battery (i.e. nickel-zinc battery using aq. KOH, as electrolyte). Examples of polymers stable to an acid environment include polyolefins, halogenated polyolefins, fluoroethylenes, such as PTFE, as well as copolymers and

SUBSTITUTE SHEET (RULE 26)

- 17 -

mixtures thereof. Examples of polymers stable to an alkaline environment include polyolefins, (polyethylene, polypropylene), polyamines, polyurethanes, polyethylene imines, polyvinyl alcohols, cellulosic materials as well as their copolymers and mixtures thereof.

The preferred materials consist of a thermoplastic, preferably at least a polyolefin, such as polyethylene or polypropylene, with or without other polymers and/or comonomers.

A more preferred material is an ultra high molecular weight polymer (UHMW polymer) such as an UHMW polyolefin (e.g. UHMW polyethylene or UHMW polypropylene), having a ZST value of 0.1 to about 1.

The UHMW polymer may be used as the sole polymer, in blends with other polymers or not at all.

When an UHMW polymer is used as a blend with other polymers, it should be present in an amount sufficient in the matrix to provide its properties to the microporous material, namely high strength and flexibility. One or more additional polymers may also be present in the matrix so long as their presence does not materially affect the properties of the microporous material in an adverse manner. The amount of the other polymer(s) which may be present depends upon the nature of such polymer(s). It is preferred that a thermoplastic be used. The preferred thermoplastic polymers which may be present are low density polyethylene, high density polyethylene, poly(tetrafluoroethylene), polypropylene, copolymers of ethylene and propylene, metallocene derived polymers, such as affinity polymers from Dow, copolymers of polyolefins with an ethylenically unsaturated monocarboxylic acid such as acrylic acid, methacrylic acid, or acrylates and methacrylates and mixtures

SUBSTITUTE SHEET (RULE 26)

- 18 -

thereof. If desired, all or a portion of the carboxyl groups of carboxyl-containing copolymers may be neutralized with sodium, zinc or the like.

The filler to be used in the sheet product of this invention should have high surface area (BET; about 20 to 950 m²/gm, preferably at least 100 m²/gm), high pore volume (BET; at least about 0.2 cc/gm; preferably at least about 1 cc/gm). The filler may be of any form, preferably of in particulate or fibrous form or mixtures of the two. The size of the ultimate (non-agglomerated) filler material should be very small having an average diameter of from about 0.01 to about 75 microns. The low end of the particle size range refers to single particles while the high end may include agglomerated or fibrous material. The particle size is preferably from about 0.01 to about 50 microns. The filler should be substantially free of large (greater than 100 microns) diameter particulate material (ultimate or agglomerate material). The filler must be inert with respect to the battery environment and must be substantially insoluble with respect to the liquids when used in forming the subject sheet product, as fully described hereinbelow.

A second filler whether porous or non porous may use if desired, such as glass or carbon fibers or mineral whiskers.

The filler(s) component can be chosen from a wide variety of materials provided the filler is inert with respect to the battery components, such as the electrolyte composition, the electrodes and the like of the battery system in which the separator is contemplated for use. The filler component must also be substantially inert with respect to the other components of the subject separator including the polymers forming the polymer mixture, the processing aid and the like. Finally, the filler component should not be electrically

SUBSTITUTE SHEET (RULE 26)

- 19 -

conductive nor electrochemically active with respect to the battery system. Fillers which meet the above criteria will depend on the type of battery system in which it will be employed (acid or alkaline), the particular components of the battery, etc. and can be readily ascertained by those skilled in this art. For example, the term "inert" would require that battery separators with alkali insoluble fillers should be used only in alkaline batteries, and acid insoluble fillers should be used only in acid batteries. If so used, the filler is not extracted by the battery electrolyte. Neutral fillers, or fillers that do not react with either acid or alkaline electrolytes, can of course be used with either acid or alkaline batteries.

Examples of materials which are suitable as fillers in an appropriate application include materials which are soluble or insoluble in water.

The material used as filler component of the subject sheet product can be selected from a variety of materials such as metal oxides and hydroxides as, for example, oxides and hydroxides of silicon, aluminum, calcium, magnesium, barium, titanium, zirconium, cerium, iron, zinc and tin; and metal carbonates as, for example, carbonates of calcium and magnesium. Carbonaceous material as, for example, carbon black, may be used in small amounts in combination with the other filler material.

As stated above, the filler must be selected with respect to the battery environment with which the subject separator is intended for use. That is to say the particulate filler must be inert with respect to such end use battery environment. Therefore, alkali insoluble particulate such as zirconia and titanium dioxide (preferred), oxides, hydroxides and carbonates of calcium, magnesium, iron, rare earth and the like should be used only in sheet products which ultimately are

SUBSTITUTE SHEET (RULE 26)

- 20 -

formed into battery separators for alkaline batteries. Similarly, acid insoluble fillers such as siliceous fillers, e.g. silica, talc, diatomaceous earth, (precipitated silica is preferred), and the like should be used only in sheet products which ultimately are formed into battery separators for acid batteries. Certain particulates can be used in either acid, alkaline or neutral battery systems and include carbon, coal dust, graphite and barium sulfate.

The processing aid of the instant compositions further improves the processability of the composition, i.e., lowers the melt viscosity, or reduces the amount of power input which is required to compound and to fabricate the composition and aids in inducing porosity. The microporous separator of the present invention is formed from an initial composition having a very high content of processing aid therein, such, at least about 60 vol. percent and preferably at least 70 vol. percent based on the initial composition, up to about 90 vol. percent based on the initial composition.

The processing aid can be soluble or insoluble in water. The preferred plasticizers are selected from organic esters, including oligomers and hydrocarbon materials. More preferred examples of the water-insoluble processing aids are such as tricresyl phosphate; and hydrocarbon materials such as petroleum oil including lubricating oils and fuel oils and natural oils such as tall oils and linseed oils. Preferred processing aids have a solubility parameters close to that of the polymer, preferably in the range of from 7.3 to about 8.4.

There are a number of water-insoluble, normally solid processing aids such as waxes which can be used alone or in conjunction with liquid processing aids.

SUBSTITUTE SHEET (RULE 26)

- 21 -

The material used to form the form stable layer of the sheet product must be a material which is inert to the battery environment and which has good tensile strength in both the machine and cross machine directions. Thus, the material can be, for example, selected from glass, polyolefins, fluoroethylenes, polyesters or polyacrylonitrile polymers or mixtures or copolymers formed with other stable monomeric units (i.e. polyacrylonitrile/polyacrylic acid copolymer; polyolefin/polyacrylic acid copolymer) when the sheet product is used to form a separator for battery utility. Layers formed from glass, polyolefins, polyamides, cellulose and the like are preferred in forming sheet products used to form separators of alkaline battery application.

The form stable layer can be in the form of a scrim, a woven or non-woven fabric, a knit material or similar product and can be formed from a continuous or non-continuous fibrous material. The fibers themselves may be porous or non porous.

The layer may be planar (that is, have substantially planar major surfaces) or patterned (that is, have patterns, e.g. elevated and depressed sections on the major surfaces). It is preferable to utilize a planar layer to assure that the layer is properly embedded into at least a portion of the body (or thickness) of the sheet product.

The layer is preferably formed from a substantially uniform, nonwoven material in the form of a scrim or fabric. The layer should have a tensile strength of at least 3 p.s.i. The particular thickness of the form stable layer is not critical. It should be thick enough to provide dimensional stability and electrolyte retention to the sheet product as desired and should be sufficiently thin so as to allow for the

- 22 -

formation of a material suitable for use in a battery. Preferably, the form stable layer should be from about 1 mil to 50 mils in thickness, depending upon the desired effect.

Further, the form stable layer may be compressible or incompressible. Preferably the layer is somewhat compressible or capable of some deflection.

Preferably, the form stable layer runs the length of the sheet product. It may be of a width that is narrower than the sheet product and may either be located along the outer edges at the sheet product or toward the center. Two or more layers may be used if necessary or desired, either adjacent each other, on opposite sides or edges or on top of each other. More preferably, the form stable layer should extend for substantially the full length and breadth of the resultant sheet product.

The form stable layer should have a porosity of at least 50% and should have an average pore diameter of greater than about 10 microns.

As described above, the form stable layer should be at least partially embedded into at least one of the major surfaces of the sheet product. Alternatively, the form stable layer may be completely embedded in the sheet product as shown in Figure 2. In Figure 2, the sheet 11 has the form stable layer 13 completely embedded in the polymer matrix 12. As another embodiment, two or more form stable layers whether formed of the same or a different material may be used and either partially or fully embedded into the opposite major first and second surfaces of the sheet product. The location and degree of embedding depends upon the desired configuration and end use of the sheet product. Preferably, the form stable layer is embedded deeply enough to bind the two layers together. Preferably, it

SUBSTITUTE SHEET (RULE 26)

- 23 -

is embedded at least 10%, more preferably about 30% to 70% into the thickness of the microporous plastic layer.

The process of forming the subject separator, as shown comprises blending and heating the components for the microporous plastic layer to form a substantially uniform admixture thereof, forming the admixture into a sheet product, embedding the form stable sheet at least partially into a surface of the sheet product such as by a calendaring process and, subsequently extracting from said sheet product at least a portion of the processing aid contained therein. In view of the amount of filler, it has been surprisingly found that the subject composition is capable of being blended into a uniform admixture and formed into a sheet product using relatively low energy.

The procedure for extraction of the processing aid from a sheet product is well known and is not meant to form a part of the present invention, per se. A single stage extraction can be used. The solvent or extraction conditions should be chosen so that the polymer and filler components are essentially insoluble. For example, when petroleum oil is to be extracted from the composite sheet, the following solvents are suitable; chlorinated hydrocarbons, such as trichloroethylene, tetrachloroethane, carbon tetrachloride, methylene chloride, tetrachloroethane, etc., hydrocarbon solvents such as hexane, benzene, petroleum ether, toluene, cyclohexane, gasoline, etc. If water soluble processing aids are to be extracted, the extraction medium can be water, ethanol, methanol, acetone, aqueous or alcoholic sodium hydroxide, potassium hydroxide, and the like.

The extraction temperature can range anywhere from room temperature up to a temperature below

SUBSTITUTE SHEET (RULE 26)

- 24 -

(preferably at least 10°C below) the melting or degradation temperature of the polymers used.

The time of the extraction will vary depending upon the temperature used and the nature of the processing aid being extracted. For example, when a higher temperature is used, the extraction time for an oil of low viscosity may be only a few minutes, whereas if the extraction is performed at room temperature, the time requirement for a polymeric processing aid can be in order of several hours. The final composition of the separator will depend upon the original composition and the degree of extraction of the processing aid from the sheet product.

When the separator is to be provided with rib members (such as for use in an acid battery) these members can be formed from the same composition as the microporous plastic layer or from other polymeric compositions which are compatible with the composition of the microporous layer. For example, other polymer compositions can be filled, unfilled or foamed polyolefins, polyvinyl chloride and the like and applied as stripes upon the surface of the sheet. Alternately, the separator sheet can be grooved or embossed to provide the channel members to permit egress of gaseous products from the battery system such as in a flooded lead acid battery. Preferably, the ribs, if present, are formed by calendaring of the exposed surface of the microporous layer. Other similar modifications such as formation of ribs, dimples or spaces in or on the form stable layer can be made in known manners. The sheet product may contain additional components such as viscosifiers, surfactants, antioxidants, colorants, wetting agents, and the like. Such materials can be incorporated in the sheet product by having them made part of the composition, or having them separately applied by spraying and the like.

SUBSTITUTE SHEET (RULE 26)

- 25 -

The separator is flexible and capable of being folded into an envelope around an electrode. The edges of such an enveloped separator can be sealed by any of the typical means for sealing such separator edges together, such as mechanical (cold pressure welding or a mechanical crimp or interlock), heat bonding, sonic welding or adhesive bonding.

The following examples are given for illustrative purposes only and are not meant to be a limitation on the subject invention, as defined by the appended claims. All parts and percentages are by weight unless otherwise indicated. The electrical resistance was measured and given below in Table I. The electrical resistance of each sheet product was determined by the direct current method as described by J. J. Lander and R. D. Weaver in Characteristics of Separators for Alkaline Silver Oxide-Zinc Secondary Batteries: Screening Methods, ed by J. Cooper and A. Fleicher, Chapter 6 modified by using 35% H_2SO_4 as the electrolyte, Hg/Hg_2SO_4 type reference electrodes, and Pt screens as the current carrying electrodes. The voltage drop across the reference electrodes was measured at 20 ma.

EXAMPLE I

A sheet product was made from a blend of 5 pounds of an UHMW polyethylene, known as GUR 415 available from Hoechst, 32 pounds silica filler and 39 pounds processing aid mineral oil (6:1 silica/polymer ratio with 70% oil). The blend was fed into an extruder and extruded through a die in the form of a continuous web. The web and a nonwoven form stable layer formed of a non-woven glass mat 10 mils in thickness were fed

- 26 -

through the nip of a calendar roll having a series of grooves in one roll so as to form ribs on the surface of the web. The overall thickness of 42.2 mils (1.06 mm), a backweb of 9.2 mils (.22mm) and a rib height of 33 mils (.838mm). The sheet product was fed through a hexane bath to extract the processing aid to a residual level of about 14%. The resulting microporous sheet product had the following characteristics:

Tensile Strength:	8.35 N/mm²
(cross machine direction)	
Porosity:	70%±5%
Puncture Resistance:	3psi
Shrinkage:	<1%
(compared by measuring the web width before and after extraction of the processing aid)	
Dimensional Stability:	Machine Direction -
(measured before and after being soaked in water and dried)	<1% shrinkage
	Cross Machine Direction -
	<1% shrinkage

A commercial separator, known as a DARAMIC 250

separator, made by the same process, and having a 2.6:1 silica to polymer ratio, had the following properties:

Tensile strength:	6.26 N/mm²
(CMD)	
Porosity:	60%±5%
Puncture Resistance:	1psi
Shrinkage:	10%
(compared by measuring web width before and after extraction of the processing aid)	
Dimensional Stability:	
Machine Direction	3-5% shrinkage
Cross Machine Direction	1-3% shrinkage

The comparison shows that the present invention

had higher porosity, less shrinkage, better puncture resistance, and tensile strength than the presently available product.

SUBSTITUTE SHEET (RULE 26)

- 27 -

EXAMPLE II

Two series of batteries were made of 3 positive and negative electrodes. The positive electrodes were enveloped with a separator. The first series of batteries were enveloped with the separator of the present invention. The second series were enveloped with DARAMIC 250 separators.

The batteries were then filled with sulphuric acid electrolyte and subjected to the SAE overcharge test at 105°F (26°C) for at least 13 weeks.

The batteries were then torn down and analyzed for characteristics and defects with the following results:

<u>Characteristic</u>	<u>Present Invention</u>	<u>Control</u>
Electrolyte (Specific Gravity)	1.282-84	1.240-1.165
Cell Voltage	2.11	2.09
Positive Plate Corrosion	Severe	Severe
Negative Plate Condition	Expanded/Buckled	Expanded/Buckled
Holes/Web	0	0
Holes/Crease	3	13
Holes/Edge	4	-
Cracks/Crease	19	35
Cracks/Edge	-	7
Cracks/Bottom	0	98
Cracks/Corner	0	9
Shorts	0	14
Total Number of Electrode/damage due to separator	26	176

The test clearly shows that the present composite separator has much better physical properties, has improved resistance to oxidation (i.e. lesser number of cracks, holes), better resistance to elevated temperatures and better overall battery performance.

SUBSTITUTE SHEET (RULE 26)

- 28 -

EXAMPLE III

The results of these tests clearly indicate that the oxidation resistance of a sheet product according to the present invention is largely independent of the amount of oil present in the sheet.

A sheet product of the present invention made according to Example I with 14% oil was tested in a Acid Corrosion Resistance Test. This test comprises placing the separator between a positive and a negative plate in acid electrolyte and maintaining the separator in constant contact with the electrodes by the use of a 5 kilogram lead block, insulated from the electrodes by a glass plate. With a direct current of 2.5 amperes flowing constantly through the set up, the terminal voltage is measured every 4 hours until such time as the voltage goes down either below 2.6 volts or drops over 0.2 volts from the previous reading. The current is then stopped. The time from starting to stopping of the current is the acid corrosion resistance duration (specific gravity of 1.300 at 20°C).

A sample was also extracted to 0% processing aid and subjected to the same test. The results were as follows:

Present Invention

<u>Processing</u>	<u>Time to Fail</u>
<u>Aid</u>	<u>Content</u>
14%	136 hours
0%	122 hours

- 29 -

EXAMPLE IV

Samples of the present invention made according to Example I were measured and compared with a DARAMIC 250 separator for acid displacement. Acid displacement is a measure of the volume of area consumed in a battery by the separator, which space otherwise would be occupied by electrolyte. The value is measured by placing a sample of a given size of separator in a given volume of electrolyte and allowing it to remain there until saturated. The volume of electrolyte is then measured in milliliters per square meter of sample. The higher the value, the more volume is consumed by separator rather than electrolyte. This is an important issue for a battery design which desires the maximum amount of electrolyte such in those batteries with limited electrolyte volume or high energy density requirements.

The results were as follows:

<u>DARAMIC 250 Separator</u>	<u>Present Invention</u>
Displaced in ml/m ² 108	72
(Sulphuric Acid Electrolyte having a specific gravity of 1.265)	

As can be appreciated from the results, the present separator provides 36 ml/m² more electrolyte than the currently available product. This provides increased capability for electrolyte retention as a result of lower electrolyte displacement as compared to a currently available commercial separator. It is believed that this is due to the higher porosity and the higher level of porous filler contained within the separator. This allows for a greater amount of electrolyte to be retained in a battery of given size than has been possible with present separators, resulting in a higher energy density and improved reserve capacity in a battery of a given size.

- 30 -

EXAMPLE V

Sets of separators made according to the invention, one set at a 1:5 polymer to filler ratio (by weight) and using 72% and 65% processing acid during formation and a second set at 1:8 polymer to filler ratio (by weight) and using 72% by 65% processing oil during formation were tested for Total Porosity and pore size distribution and compared with a commercially sample of DARAMIC 250 separator. The results below clearly show the superior porosity and pore size distribution obtained by the present invention.

EXAMPLE VI

A sheet product was made by initially forming a blend of 13 parts high density polyethylene (Paxon FD 60, weight average molecular weight of 250,000), 55 parts titanium dioxide (Unitane OR-573; density 4.3 BET surface area 280 m²/cc, BET pore volume 0.35 cc/g), 30 parts of a hydrocarbon mineral oil and 1 part carbon black. The initial blend was formed with a Hobart mixer. The material was then subjected to a twin screw extruder having five heating zones (180°C/185°C/190°C/195°C/200°C) and extruded as pellets which were passed through two 40 mesh (U.S. Std) screens to remove any large agglomerates.

The pelletized polymer/filler composition was passed through a second extruder having the same five heating zones and an eight inch sheeting die (heated 200°C) capable of forming sheet material of approximately 25 mils thick. The extruder was run at 50 rmp screw speed, torque of 32% and 650 psi pressure.

The formed sheet was passed through a set of heated calendaring rollers in conjunction with a 6 mil

SUBSTITUTE SHEET (RULE 26)

- 31 -

non-woven polypropylene fibrous sheet (Typar T520) at 66-77°C under 50 psi at a take-off rate of 6.3 ft./min. and then over three cooling rollers. The sheet product was immersed in 1, 1, 1-trichloroethane for 30 minutes, air dried and then immersed in a second bath of trichloroethane for 30 minutes and again air dried to remove approximately 95% of the hydrocarbon oil. The sheet product was 9 mil thick and, by microscopically examination, was observed to have approximately 80% of the polypropylene sheet embedded in the polymer/filler matrix and had both macroporosity and microporosity and had a maximum pore size of 0.38 μm .

The sheet was analyzed for electrical resistivity (in 30% KOH), porosity, puncture strength and tensile strength. The results were ER=15 ohm-cm; 41% porosity; 7.7 lb puncture strength; and 2700 psi tensile strength/55% elongation.

While the present invention has been described in relation to its preferred embodiments, other embodiments, modifications and equivalents can be used. It is the intent of the present claims to cover all embodiments, modifications and equivalents as follow within the true scope and spirit of the present invention.

- 32 -

WHAT IS CLAIMED:

1. A sheet product comprising a plastic microporous matrix formed of a substantially homogenous blend of a thermoplastic polymer, an inert filler and a processing aid, wherein the ratio (by weight) of polymer to filler is from about 1:4 to about 1:50; and a porous form stable layer at least partially embedded in one surface of the plastic matrix.

2. The sheet product of Claim 1 wherein the porous layer is a fibrous layer in the form selected from the group consisting of woven, nonwoven knit and braided fabrics, and wherein the fibers are selected from polyesters, polyolefins, polynitriles, amines and glass and the layer has a tensile strength of at least 3 psi.

3. The sheet product of Claim 1 wherein the polymer is a polyolefin.

4. The sheet product of Claim 1 wherein the filler is selected from an inert, high surface area, high pore volume inorganic material said filler having an average particle size of from about 0.01 to 50 microns and is substantially free of particles having particle size larger than 100 microns and wherein the ratio of polymer to filler (by weight) is from about 1:4 to about 1:10.

5. The sheet product of Claim 1 wherein the filler is a siliceous filler.

6. The sheet product of Claim 1 wherein the filler is selected from oxides and hydroxides of calcium, magnesium, titanium or aluminum and mixtures thereof.

7. A battery separator comprising a microporous sheet product formed of a polymeric matrix of a substantially uniform mixture of an ultrahigh molecular

- 33 -

weight polymer and an inert filler wherein the ratio (by weight) of polymer to filler is from about 1:4 to 1:50 and a porous form stable layer at least partially embedded in either a first or second major surface of the polymeric matrix.

8. The battery separator of Claim 7 wherein the polymer is selected from the a group consisting of ultra high molecular weight polyolefins and halogenated olefins.

9. The battery separator of Claim 7 wherein the form stable layer is substantially embedded within the polymeric matrix.

10. The battery separator of Claim 7 wherein the polymeric matrix comprises a blend composed of from about 65 to 99.9 weight percent of a filler, from about 0.1 to 15 weight percent of an ultra high molecular weight polymer and from 0 to about 15 weight percent of a processing aid.

11. The battery separator of Claim 10 wherein the polymer matrix comprises from about 80 to 98.5 weight percent filler, from about 1.5 to 10 weight percent polymer and from 0 to about 10 weight percent of processing aid.

12. The battery separator of Claim 7 wherein the particulate filler is selected from oxides and hydroxides of calcium, magnesium, titanium, aluminum, oxides of silicon and mixtures thereof.

13. The battery separator of Claim 7 wherein the ratio of polymer to filler (by weight) is from about 1:4 to about 1:10.

14. The battery separator of Claim 13 wherein the ratio (by weight) of polymer to filler is from about 1:6 to about 1:10.

15. In a battery having a case, at least one pair of electrodes of opposite polarity, an electrolyte

SUBSTITUTE SHEET (RULE 26)

- 34 -

composition and a separator positioned between adjacent electrodes of opposite polarity, wherein the improvement comprises that the separator extends at least the length and breadth of the electrodes and comprises the product of Claim 1.

16. In a battery having a case, at least one pair of electrodes of opposite polarity, an electrolyte composition and a separator positioned between adjacent electrodes of opposite polarity, wherein the improvement comprises that the separator extends at least the length and breadth of the electrodes and comprises the product of Claim 7.

17. A battery separator comprising a microporous sheet product having a thickness of less than about 50 mils bound by first and second major surfaces of the sheet product, comprising a substantially uniform mixture of a polymer selected from the group consisting of high density polyolefins, ultra high molecular weight polyolefins and blends thereof and an inert filler wherein the ratio of polymer to filler (by weight) is from about 1:4 to 1:10 and having a porous form stable sheet embedded in at least one of the first and second major surfaces, and having porosity throughout the sheet product's thickness.

18. The battery separator of Claim 17 wherein the ratio of polymer to filler is from about 1:4 to about 1:10, the filler is selected from a high surface area, high pore volume inorganic material, the filler having an average particle size of from about 0.01 to 50 microns and is substantially free of particles having particle size larger than 100 microns.

19. The battery separator of Claim 17 wherein the form stable layer is a woven, non-woven, knit or braided fabric and the sheet product has a total void volume of at least about 60 volume percent.

20. A battery separator comprising a composite sheet product having a first microporous thermoplastic

SUBSTITUTE SHEET (RULE 26)

- 35 -

layer, the first layer having an inert filler present in a ratio of polymer to filler (by weight) from about 1:4 to 1:50; a second porous fibrous form stable layer at least partially embedded in a surface of the first layer and wherein of the composite sheet has a gradient of pore structures such that pores in the first layer are microporous and average less than 1 micron in diameter, the pores in the form stable layer are microporous and average greater than 10 microns in diameter and the pores in the area where the first and second layers meet are a series of extended elongated microporous pores.

21. A battery separator for a recombinant battery comprising:

a.) a microporous layer formed of a polyolefin, an inert filler and a processing aid, wherein the amount of polymer to filler in the layer is in a ratio (by weight) of from about 1:20 to about 1:50 and the processing aid is present in an amount of from about 0 to about 15% by weight; and

b.) a porous form stable layer at least partially embedded into a first major surface of the first layer;

and wherein the porosity (by volume) of separator is from about 85% to about 98%.

22. A battery electrode comprising:

a.) a grid having a first and second major surface;

b.) active material covering the major surfaces of the grid; and

c.) one or more separators partially embedded into the active material of the first and second major surfaces, wherein the separator is formed of a first microporous, siliceous filled, thermoplastic layer and a second porous, form stable layer bonded to the first layer and wherein the second layer of the separator is

- 36 -

embedded into the active material of the electrode.

23. The electrode of Claim 22 wherein the form stable layer is formed of a non woven glass mat and the thermoplastic layer is formed of a polyolefin and silica wherein the ratio (by weight) of polymer to silica is from about 1:4 to about 1:10.

24. The electrode of Claim 22 wherein the electrode is a positive electrode.

25. The electrode of Claim 22 wherein the electrode is a negative electrode.

26. A process for forming an electrode/separator combination comprising the steps of:

- a.) taking an electrode grid;
- b.) applying an active material in paste form to the outer surfaces of the grid,
- c.) partially embedding one or more separators into the active material; and
- d.) drying the electrode/separator combination; wherein the separator is formed of a composite sheet material comprising a first microporous layer of a thermoplastic polymer and an inert filler and a second, porous form stable layer partially embedded into a major surface of the first layer.

27. A separator for alkaline batteries comprising a polymer matrix formed of one or more thermoplastic resins, one or more alkaline electrolyte resistant inorganic fillers wherein the ratio of polymer to filler (by weight) is from 1:4 to 1:50 and a porous, formstable layer at least partially embedded into a major surface of the polymer matrix.

28. The separator of Claim 27 wherein the filler is selected from the group consisting of oxides and hydroxides of calcium, magnesium, titanium or aluminum and mixtures thereof, the polymer is selected from the group consisting of polyolefin homopolymers, polyolefin copolymers and blends thereof, and the form stable layer

SUBSTITUTE SHEET (RULE 26)

- 37 -

is a fibrous layer in the form selected from the group consisting of woven, nonwoven knit and braided fabrics, and wherein the fibers are selected from polyesters, polyolefins, polynitriles, amines and glass and the layer has a tensile strength of at least 3 psi.

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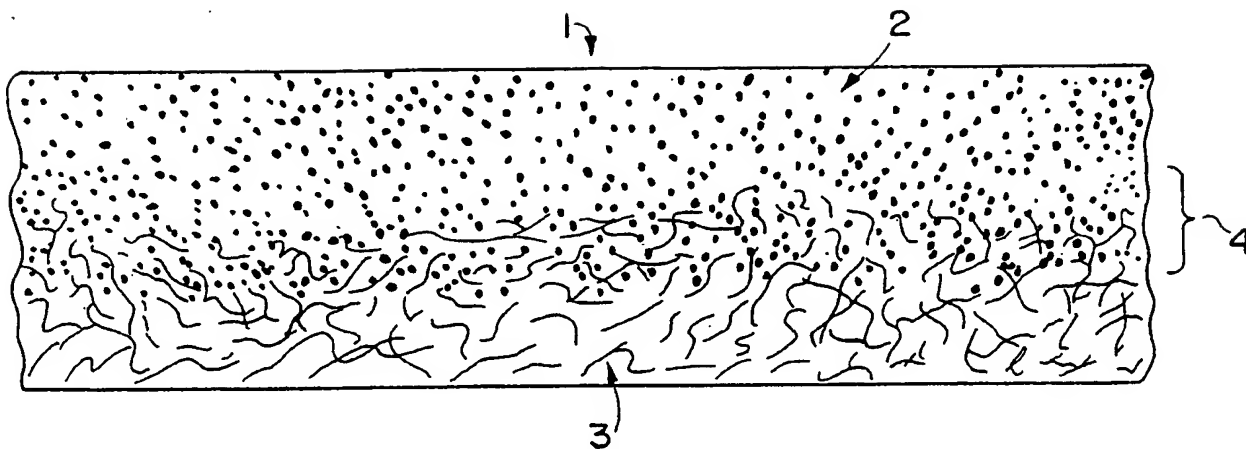


FIG. 1

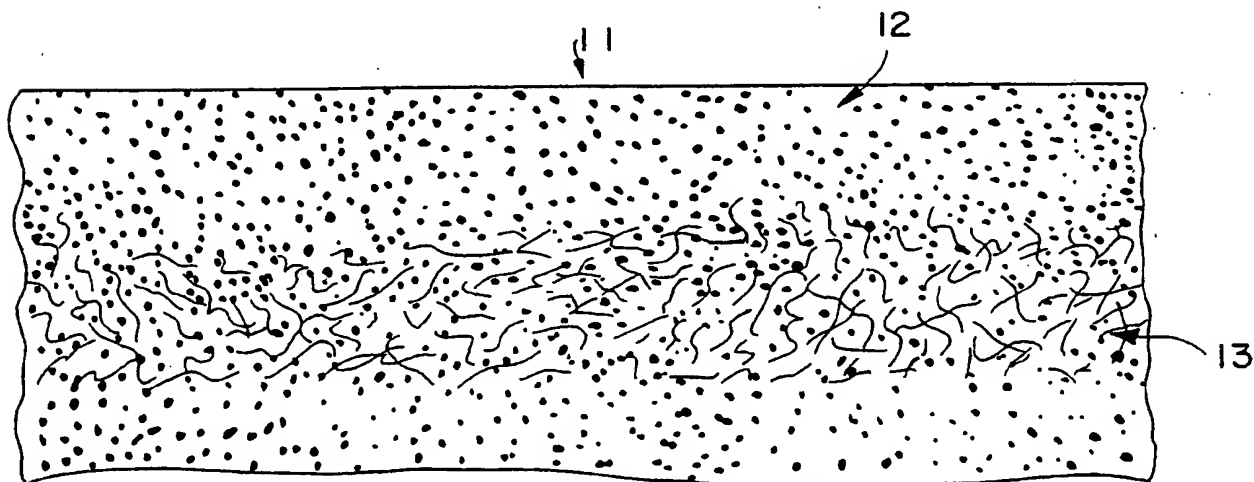


FIG. 2



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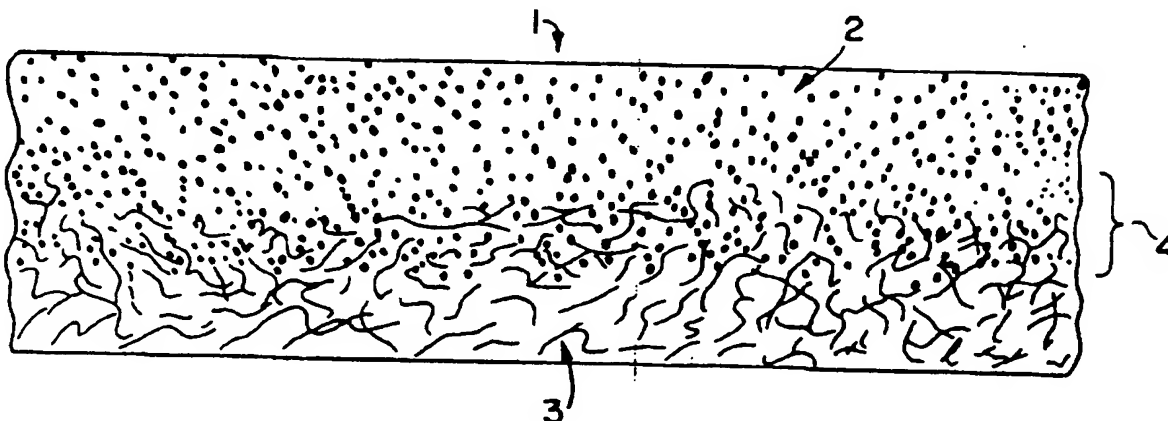
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(57) Abstract

A battery separator composed of a microporous, composite sheet product having first and second major surface, formed from a uniform mixture of a polymer, a filler, a processing aid, a porous form stable layer at least partially embedded in either the first or second major surface. The weight ratio of polymer to filler is from about 1:4 to 1:50; preferably about 1:4 to 1:10.

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INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	see the whole document	
Y	DE, A, 14 96 123 (W. R. GRACE & CO.) 13 March 1969 * PAGE, LINE 1 - PAGE 2, LINE 19; PAGE 3, PARAGRAPH 2 - PAGE 4, PARAGRAPH 1; PAGE 4, PARAGRAPH 3 - PAGE 11, PARAGRAPH 2; PAGE 14, PARAGRAPH 3 - PAGE 15, PARAGRAPH 3; PAGE 20, PARAGRAPH 2 - PAGE 22, PARAGRAPH 2; EXAMPLES 1 - 20; PAGE 44, PARAGRAPHS 1 - 2; CLAIMS 1 - 9, 11 - 19 *	1-8, 10-28
X, Y	US, A, 5 180 647 (B.J. ROWLAND ET AL.) 19 January 1993	1-19, 27, 28 20-26
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 94/02130

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. Claims: 1-21, 27-28
2. Claims: 22-26

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 94/02130

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